Contents

ACCSP Heron Island - Wistari CO2 mooring

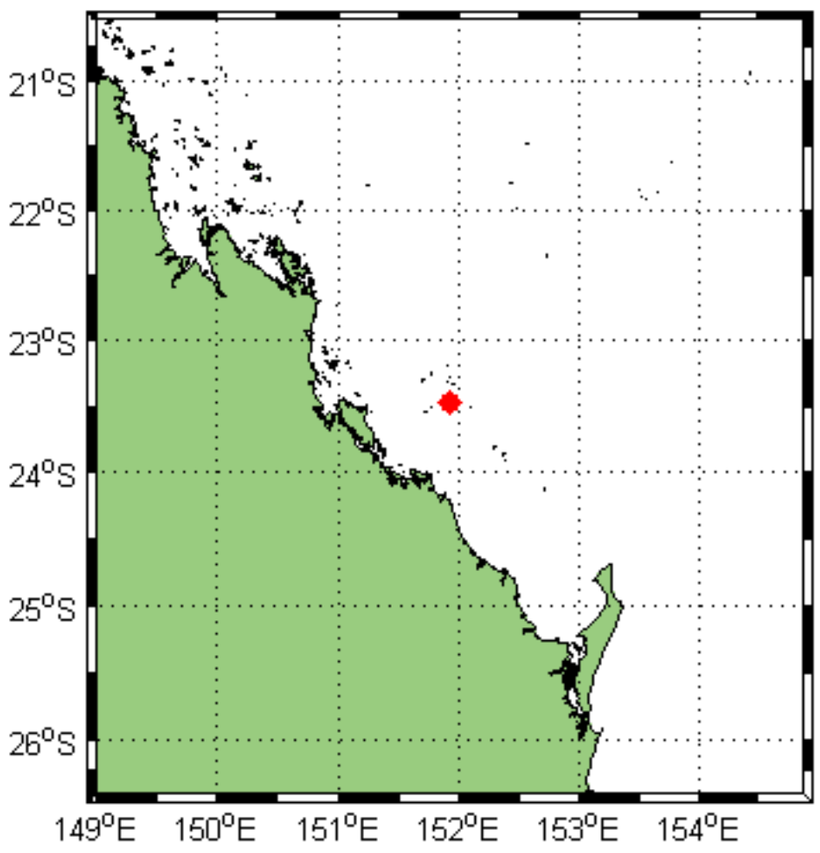
Dataset:

```
09FS20110311_heron_4.txt
```

Deployment information

Location:

```
Heron Island - Wistari Channel, Queensland;-23.4223,151.6911
```



Water Depth:

```
16m
```

Platform:

```
IMOS_ANMN-AM_CO2_GST
```

Platform code:

```
GBRWIS
```

Deployment code:

```
GBRWIS_4
```

Start date

```
20110310T160000Z
```

End date

```
20110819T220000Z
```

Mooring Bounds: North West South East

```
-24.34385     -22.50077      145.7229      157.6593
```

Data history

Data report submission:

```
01/02/2016
```

Most recent report update:

```
01/02/2016
```

Investigators:

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Christopher Sabine, NOAA-PMEL, 7600 Sand Point Way NE, Seattle WA 98115 USA

Mooring deployment

Deployed

```
10/03/2011 23:55
```

Recovered

```
19/08/2011
```

Vessel

```
Heron Island Mooring
```

Moored sensors:

Battelle MApCO2 s/n

```
0115
```

Seabird SBE 16pus_V2 s/n

```
01606552
```

Aanderaa Optode s/n

```
1450
```

Field personel

```
Erik van Ooijen,Phil deBoer,Curt Chalk,Craig Neill
```

Instrumentation

```
Erik van Ooijen
```

Quality control

```
Erik van Ooijen
```

Data file description:

Variable [Unit] *Description* ==========

TIME [YYYY-MM-DDThh:mm:ssZ] *Time and Date, ISO8601*

LATITUDE [degr] _Latitude

LONGITUDE [degr] _Longitude

XCO2_DRY_SW [µmol/mol] *Mole fraction of CO2 in the equilibrator head space*

XCO2_DRY_AIR [µmol/mol] *Mole fraction of CO2 in the atmosphere*

fCO2_WET_SW [µatm] *Fugacity of carbon dioxide at surface water, corrected for water vapour at surface water salinity and temperature*

DfCO2 [µatm] *Delta fCO2 = (fCO2_WET_SW - fCO2_WET_AIR)*

ATMOSPHERIC PRESSURE [kPa] *Atmospheric pressure*

EQUILIBRATOR PRESSURE [kPa] *Equilibrator pressure*

SEA SURFACE TEMPERATURE [degC] *Sea surface temperature*

EQUILIBRATOR TEMPERATURE [degC] *Equilibrator temperature*

SALINITY [PSS] *Sea surface salinity*

DISSOLVED_OXYGEN [µmol/l] *Concentration O2 in surface sea water*

WOCE QC flag *2=good, 3=questionable, 4=bad*

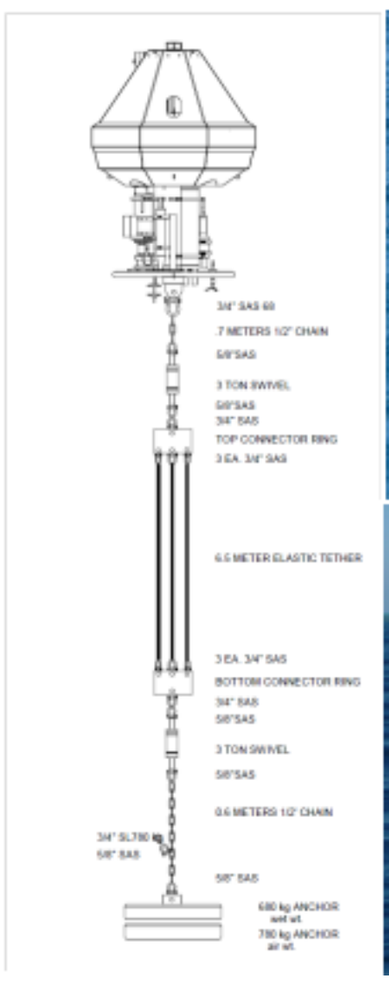
SUB_FLAG *24-bit number, internal QC*

General system description and procedures

Instrumentation and methods

Measurements are made with a Battelle Seaology pCO2 monitoring system (MApCO2), a Seabird SBE16plusV2 CTD, mounted on a surface buoy similar to the system described in Sutton et al. (2014), with an Aanderaa optode used to measure dissolved oxygen concentrations. The seawater sensor intakes for the MapCO2, SBE16Plus V2 and the optode are located at about 1m water depth. The CO2 measurement uses a bubble equilibrator (Sutton et al., 2014), where the air from the equilibrator headspace is circulated through a LI-COR 820 non-dispersive infrared detector (NDIR) for measurement of CO2. The system carries out an automated measurement sequence every 2 or 3 hours, depending on the instrumentation setup. At the beginning of each measurement sequence, the NDIR undergoes a two point calibration with a zero CO2 gas and a high CO2 standard span gas (typically 450-550 micromol/mol), which bracket the range of CO2 mole fractions in seawater and air. The zero CO2 gas is generated by cycling air through a soda lime chamber and silica gel to remove CO2 and water vapour, respectively. The CO2 span gas is prepared by the NOAA Earth Systems Research Laboratory in the USA and calibrated on the WMO X2007 scale with a standard deviation of 0.06 micromol/mol (http://www.esrl.noaa.gov/gmd/ccl/airstandard.html). Each measurement cycle of zero and span gas, equilibrator headspace, and air takes 20 minutes with the equilibrator headspace measurement occurring at about 17 minutes followed by the air measurement. The pressure measurements are considered the same for the equilibrator headspace gas and air measurements due to the design of the MapCO2 system (Sutton et al., 2014) as are the temperature and salinity of the surface seawater and the equilibrator measured by the Seabird SBE16PlusV2.

Location and mooring design



The Heron Island Wistari mooring is located on the east side of Heron Island in the Wistari Channel in about 16m water depth. A 700kg anchor holds the mooring buoy in position, which is connected to the surface buoy via a 16.5m bungee used to dampen wave action. As part of regular maintenance and to minimise the effects of biofouling, the mooring is recovered every six months, the mooring line checked and replaced if necessary, and a replacement surface buoy and newly calibrated sensors swapped in.

Testing and calibration procedures

The LI-COR 820 sensor response is checked before and after each deployment using a range of CO2-in-air reference gases (0, 260, 370, 450 micromol/mol) at CSIRO, Hobart. The sensor measurement using factory calibrations for the LI-CO2 820 is typically within 1 micromol/mol of the reference gas value. If the LI-COR 820 measurements and the CO2-in-air reference gas values are different by more than 2 micromol/mol, a correction is applied to Li-CO2 820 output based the reference gas values. A seawater bath operated over a range of temperatures and CO2 expected in the field is then used to check the MapCO2 system (equilibrator and LI-COR 820 measurement) against a General Oceanics 8050 CO2 sensor to ensure the systems agree within 2 micromol/mol. Pressure measurements are made using the LI-COR 820 pressure sensor, checked against a Druck DPI142 pressure indicator and verified to agree within 0.5 kPa before and after each deployment. The air CO2 values are compared to Globalview CO2 products, although these can result in some variability due to limited data in Globalview to constrain atmospheric boundary layer CO2 measurements in coastal regions of the Southern Hemisphere.

A SBE16plus V2 CTD is polled for the temperature, salinity, and dissolved oxygen data for each MApCO2 measurement sequence, with additional measurements made each hour. The SBE16PlusV2 temperature and salinity measurements use either factory calibrations for initial deployments, or annual calibrations performed at a certified National Australian Testing Authority facility at CSIRO, Hobart. The optodes are calibrated before and after deployments at CSIRO, Hobart, using a purpose built calibration system, referenced to dissolved oxygen measurements made using modified Winkler titrations (Culberson, 1991). The calibrations cover a range of temperatures and oxygen concentrations that occur in the field and new calibration coefficients are generated to fit a Stern-Volmer equation (Uchida et al., 2008).

Data reduction and quality control

Fugacity

After recovery of the instrument the data from the MApCO2 and the SBE16plus is downloaded. The data are recorded at each 2 or 3 hourly measurement interval as blocks of measurements of equilibrator headspace gas, air, zero and span gas values. The data blocks are checked for size and the MApCO2 data is checked for outliers and corrected using the Thomson Tau method (Thompson, 1985).

The NDIR detection is based on the absorption of infrared light by CO2. For each measurement cycle, the zero and span gas are analysed immediately before equilibrator air or atmospheric gas measurements to calibrate the LI-COR 820 NDIR response and provide a measurement of the CO2 mole fraction in the gas stream. The gas stream analysed by the NDIR is only partially dried by flowing the gas through silica gel and the same light absorbed by CO2 is also absorbed by water vapour present in the gas. A dilution correction is applied to account for the presence of water vapour that is measured in the gas using a humidity sensor (LI-COR Application note 129):

$$xCO_2 = \frac{xCO_2^{raw}}{(1 - w/1000)}$$

where w is calculated water vapour mole fraction and xCO2raw is the raw data value for the CO2 mole fraction measured in the gas stream by the LI-COR 820 NDIR.

The partial pressure of CO2 in the water is calculated by applying a water vapour pressure correction:

$$pCO_2 = xCO_2(P - p[H_2O])$$

with,

$$p[H_2O] = \exp 24.4543 - 67.4509\frac{100}{T} - 4.8489 \ln \frac{T}{100} - 0.000544S$$

the calculated water vapour pressure of the equilibrator sample at the sea surface temperature, *T (K)*, and Salinity, *S* (Weiss and Price, 1980) and *P* is the total pressure in atmospheres.

The partial pressure of CO2 is converted to fugacity using (Weiss, 1974):

$$fCO_2 = pCO_2 \exp \frac{P(B(CO_2, T) + 2(1 - xCO_2)^2\delta(CO_2, T))}{RT}$$

where, $R = 82.0578 cm^3 mol^{-1} K^{-1}$, $B(CO_2, T) = -1636.75 + 12.0408T - 3.27957 \cdot 10^{-2}T^2 + 3.16528 \cdot 10^{-5}T^3$ and, $\delta(CO_2, T) = 57.7 - 0.118T$

Dissolved oxygen

Two voltage signal (*V0* and *V1*) related to the bphase (*Bp*) and the temperature (*Topt*, in degrees Celsius) by:

$$Bp = 12V0 + 10; Topt = 9V1 - 5$$

from the Aanderaa optode are measured and stored by the SBE16plus. From these values a pre- and post-calibrated dissolved oxygen values (*DOraw*) are calculated using the Stern-Volmer equation (Uchida et al., 2008), and the corresponding pre- and post- calibration coefficients (Appendix 3);

$$DO_{raw} = \frac{(c4 + c5Topt)/(c6 + c7Bp) - 1}{c1 + c2Topt + c3Topt^2}$$

This value for dissolved oxygen applies to use in fresh water and therefore needs to be compensated for seawater salinity using:

$$DO_{sc} = DO_{raw} \exp S(B0 + B1T_S + B2T_S^2 + B3T_S^3) + C0S^2$$

With *S* the salinity obtained by the SBE16plus and

$$T_S = \ln \frac{298.15 - T}{273.15 + T}$$

With T the temperature obtained in Celsius by the SBE16plus, and B0 = -6.24097e-3, B1 = -6.93498e-3, B2 = -6.90358e-3, B3 = -4.29155e-3, C0 = -3.11680e-7.

Subsequently, a drift correction of 1.61% per year is applied from the calibration data for each of the pre- and post-calibrated and salinity compensated values. From these values an average value for the dissolved oxygen (DO) and a standard deviation (SD_DO) is obtained, which is interpolated at the time when the MApCO2 equilibrator pump off cycle ends.

Data report

Automated data quality control report:

For first order quality control, automated checking of value ranges for a number of diagnostic parameters are checked, and subflags assigned to values outside the accepted ranges listed in Appendix 2. The summary results of the automated data checking procedure were:

Flagged data points:

```
> MAX SD_XCO2_EQUIL_PUMP_ON
2011/04/28,04:00:00
XCO2 Span pump off or post cal out of range
2011/03/24,08:00:00
2011/04/20,04:00:00-2011/04/20,08:00:00
2011/04/21,20:00:00-2011/04/21,22:00:00
2011/06/15,12:00:00
```

Delayed mode quality control report:

After automated checking, data are plotted and manually checked in a final delayed mode quality control with WOCE (http://cchdo.ucsd.edu/formats) quality flags used, where 2=good, 3=questionable, 4=bad, with the following result:

```
No issues
```

Low salinity values are verified using NRS data at MAI site (http://www.csiro.au/tasman/nrsweb/) and BOM flood history data (http://www.bom.gov.au/tas/flood/flood_history/flood_history.shtml).

Final data quality summary:

Parameter	% flag = 2 good	Number Points
fCO2 sea water	99.587416	1931
XCO2 atmosphere	99.638989	1932
Sea Surface Temperature	100.000000	1939
Sea Surface Salinity	100.000000	1939
Dissolved Oxygen	100.000000	1939

Data summary:

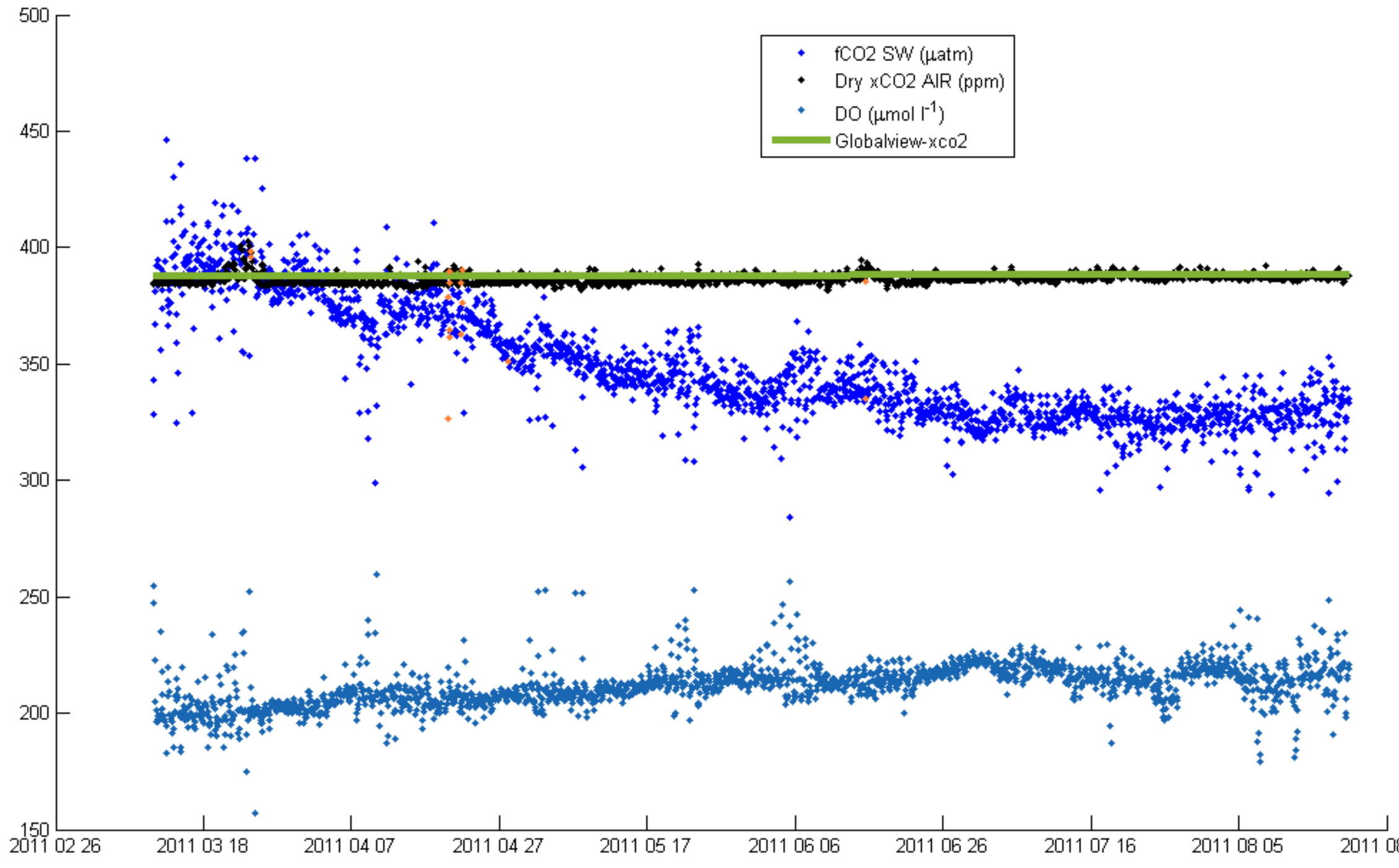


Figure 1: xCO2 (ppm) for air, fCO2 (µatm) and Dissolved Oxygen (DO; µmol/l) for sea water. The red and orange data points represent bad (flag =4) and questionable (flag = 3) data, respectively.

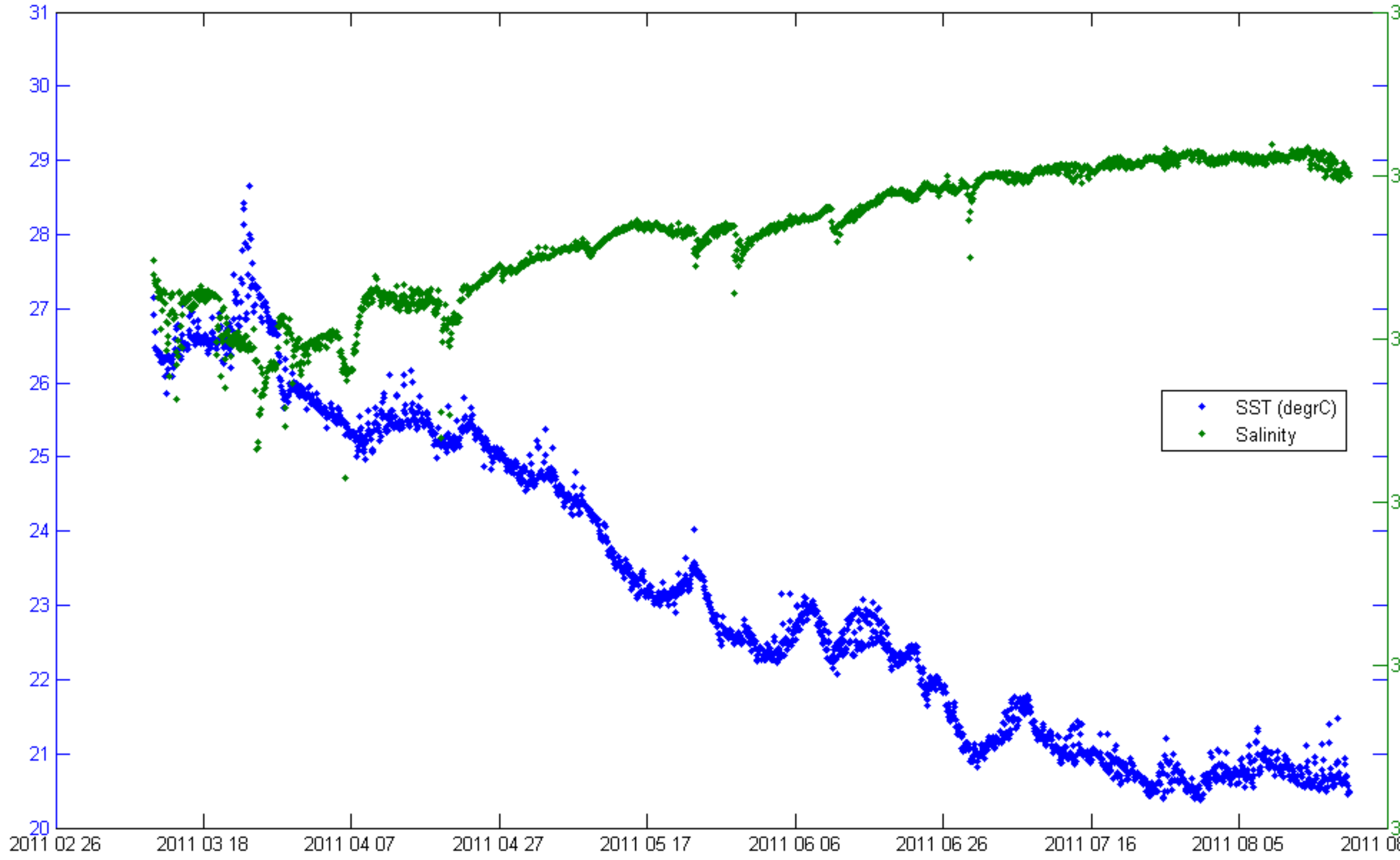


Figure 2: Temperature and salinity.

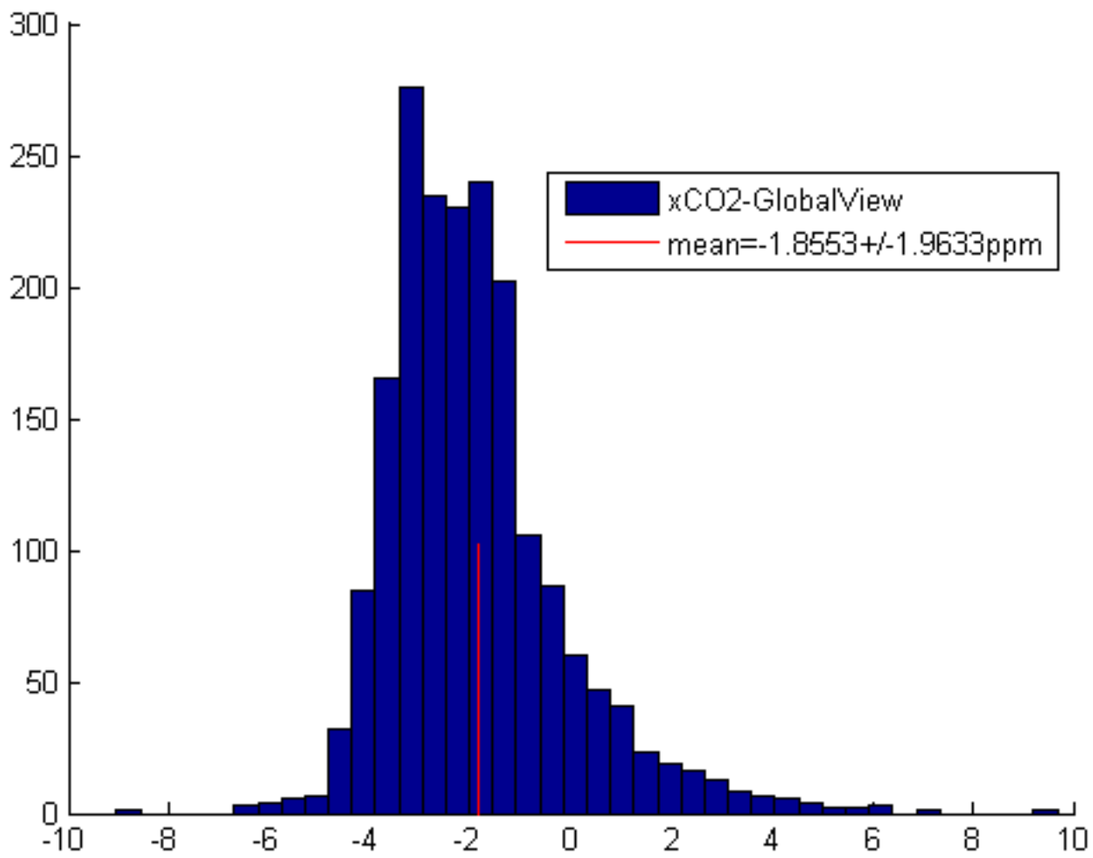


Figure 3: Histogram of atmospheric xCO2 - Global view xCO2

Appendix 1: Instrumentation specifications

Seaology pCO2

```
MANUFACTURER:Battelle Memorial Institute, Columbus, Ohio, USA
WEBSITE: http://battelle.org/our-work/national-security/maritime-systems
MODEL: Seaology
SERIAL NO: 0115
FIRMWARE VERSION: 3.99
EQUILIBRATOR DESIGN: Bubble Equilibrator
EQUILIBRATOR VOLUME: Less than 100 ml of air equilibrating with an unlimited volume of seawater
HEADSPACE GAS FLOW RATE: ~600 cc/min
VENTED: yes
INTAKE DEPTH: 1m
MEASUREMENT METHOD: Absolute, non-dispersive infrared (NDIR) gas analyser
```

CO2 and Equilibrator and Air Pressure Sensor:

MANUFACTURER:LI-COR, Lincoln, Nebraska, USA
WEBSITE: http://www.licor.com/env/
MODEL: LI-820
CO2 RESOLUTION: 0.1 µmol/mol
CO2 UNCERTAINTY: < 2 µmol/mol based on comparisons in the laboratory
before and after deployment with four WMO X2007 referenced gas standards (0, 260, 370, 450 µmol/mol)
and < 2 µmol/mol based on pre-deployment comparison in the laboratory with equilibrator headspace
measurements of seawater made using a General Oceanics model 8050 pCO2 measurement system (General Oceanics, Miami, Florida, USA).
PRESSURE RESOLUTION: 0.01 KPa
PRESSURE UNCERTAINTY: < 0.5 KPa, Based on laboratory comparison against Druck DPI 142 pressure indicator
CALIBRATION DATE: Unknown

Relative Humidity Sensor:

MANUFACTURER:Sensirion Humidity Sensor, USA
WEBSITE: http://www.sensirion.com
MODEL: SHT71
MEASUREMENT RANGE: 0-100%
ACCURACY: +/- 3% (20-80% RH)
CALIBRATION: Factory calibration before purchase

CO2 Span Gas:

MANUFACTURER:NOAA Earth Systems Laboratory, USA
CYLINDER NUMBER: JB02724
GAS CYLINDER PRESSURE, PRE-DEPLOYMENT: 2000 psi
GAS CYLINDER PRESSURE, POST-DEPLOYMENT: Unknown psi
CO2-IN-AIR CONCENTRATION (WMO X2007): 509.15 PPM
CALIBRATION DATE: 2009-07-14

O2 Sensor:

MANUFACTURER:Aanderaa, Norway
WEBSITE: http://www.aanderaa.com/
MODEL: 1450
SERIAL NO: 4175C
FOIL BATCH NO: 5009
RESOLUTION: <1 µM
UNCERTAINTY: < 1 µmol/l, based on Winkler oxygen titrations at CSIRO, Hobart
CALIBRATION DATE:PRE-DEPLOYMENT: 30-Nov-2010 POST-DEPLOYMENT: 29-Nov-2011

CTD Sensor (Equilibrator and Sea Surface):

MANUFACTURER:Sea-Bird Electronics, Bellevue, Washington, USA
WEBSITE: Sea-Bird Electronics, Bellevue, Washington, USA
MODEL: SBE 16plusV2_seacat
SERIAL NO: 01606552
RESOLUTION: 0.0001 °C; 0.00005 S/m
UNCERTAINTY: 0.005 °C; 0.0005 S/m
CTD DEPTH: 1 m
CALIBRATION DATE: 09-Apr-10, factory calibrated before purchase.

Appendix 2: Range limits

Range limits for assigning flags to instrument diagnostic parameters. Values outside the ranges are automatically flagged as bad. Max SD is the maximum standard deviation of all readings at each measurement time.

Variable Min Max

Span Value Deviation -5 5
Zero Value Deviation -5 5
Delta pressure Atmosphere 5 9
Delta pressure Equilibrator 5 9
Max SD XCO2 EQUIL PUMP ON 10
Max SD xCO2/ pCO2/ fCO2 2
Max SD_PRESS_LICOR_EQUIL_PUMP_OFF 0.05
MAX SD_PRESS_LICOR_AIR_PUMP_OFF 0.1
MAX SD_TEMP_LICOR air/equil/span 0.1
MAX SD_RH_AIR_PUMP_OFF 1
MAX SD_RH_EQUIL_PUMP_OFF 1
MAX SD_RH_TEMP_AIR_PUMP_OFF 0.05
MAX SD_RH_TEMP_EQUIL_PUMP_OFF 0.05
MAX SD_RH_SPAN_PUMP_OFF 2
MAX SD_RH_TEMP_SPAN_PUMP_OFF 0.05
SBE Temparature -2 40
SBE Salinity 0 42
Optode DO 100 400

Appendix 3: Instrument calibration coefficients

Oxygen optode calibrations coefficients for optode 4175C serial number 1450 foil number 5009:

Coefficient	Pre-deployment	Post-deployment
C1	0.0029091	0.0027579
C2	0.00012693	0.00011955

```
C3    2.1443e-06    2.0051e-06
C4    232.79    232.83
C5    -0.24559    -0.26305
C6    -39.943    -39.274
C7    4.0443    4.043
```

```
Seabird SBE16plus V2, serial number 01606552 calibration coefficients:
```

```
Temperature    Coefficient
TA0    0.0012896
TA1    0.00025733
TA2    7.9564e-08
TA3    1.3432e-07
TOFFSET    0
```

```
Salinity    Coefficient
G    -1.0569
H    0.14229
I    -0.00023772
J    3.605e-05
CPCOR    -9.57e-08
CTCOR    3.25e-06
CSLOPE    1
```

Additional information:

The CO2/acidification mooring at the Heron Island was funded through and Ocean Carbon and Acidification project of the Australian Climate Change Science Program awarded to BT. Users of these data are requested to cite the data source as below and to send copies of manuscripts to the PI prior to submission to ensure data are accurately represented.

Citation:

We rely on users of these data to recognise the effort required to obtain data by citing these data as:

B. Tilbrook, E. van Ooijen, C. Neill, A. Sutton and C. Sabine (2009) Ocean and atmosphere fCO2 timeseries measurements from Wistari Channel, Heron Island, Australia. http://imos.aodn.org.au/imos123/.

References

Alliance for Coastal Technologies (2010) Performance Demonstration Statement, PMEL MAPCO2/Battelle Seaology pCO2 Monitoring System, UMCES Technical report Series: Ref. No. [UCMES]CBL 10-092, URL: http://www.act-us.info/Download/Evaluations/pCO2/PMEL_MAPCO2_Battelle_Seaology/

LI-COR Application Note 129. The Importance of Water Vapor Measurements and Corrections, URL: http://www.licor.com/env/applications/gas_analysis.html

Thompson, R. (1985) A Note on Restricted Maximum Likelihood Estimation with an Alternative Outlier Model. Journal of the Royal Statistical Society. Series B (Methodological),47(1), 53-55.

Uchida, H., T. Kawano, I. Kaneko and M. Fukusawa (2008) In situ Calibration of Optode-based Oxygen Sensors. Journal of Atmospheric and Oceanic Technology, 25, 2271-2281.

Culberson, C. H., (1991). Dissolved oxygen. WHP Operations and Methods, WHPO 91-1, WHP Office, Woods Hole Oceanographic Institution, Woods Hole, Mass. U.S.A.

Weiss, R. F. (1974) Carbon dioxide in water and seawater: the solubility of non-ideal gas. Marine Chemistry, 2, 203-215.

Weiss, R.F. and B. A. Price (1980) Nitrous oxide solubility in water and seawater. Marine Chemistry, 8, 347–359

A. J. Sutton, C. L. Sabine, S. Maenner-Jones, N. Lawrence-Slavas, C. Meinig, R. A. Feely, J. T. Mathis, S. Musielewicz, R. Bott, P. D. McLain, H. J. Fought, and A. Kozyr (2014) A high-frequency atmospheric and seawater pCO2 data set from 14 open-ocean sites using a moored autonomous system. Earth System Science Data, 6, 353-366. doi:10.5194/essd-6-353-2014.

Cooperative Global Atmospheric Data Integration Project. 2013, updated annually. Multi-laboratory compilation of synchronized and gap-filled atmospheric carbon dioxide records for the period 1979-2012 (obspack_co2_1_GLOBALVIEW-CO2_2013_v1.0.4_2013-12-23). Compiled by NOAA Global Monitoring Division: Boulder, Colorado, U.S.A. Data product accessed at http://dx.doi.org/10.3334/OBSPACK/1002

Attachments

```
No attachments
```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